Form PTO-1390 (Rev. 12-29-99) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO. **H 3243 PCT/US**

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/857635

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/09404	**December 2, 1999**	**December 9, 1998**

TITLE OF INVENTION

AGENT AND METHOD FOR SEALING OR CONSOLIDATING ROCK, LOOSE ROCK OR SOILS, ESPECIALLY BORE HOLES

APPLICANT(S) FOR DO/EO/US

Ilona Lange, Wolfgang Breuer, Claus-Peter Herold, Stephan Von Tapavicza and Dark Mill

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.

2. □ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.

3. □ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).

4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.

5. ■ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. □ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau.
   c. □ is not required, as the application was filed in the United States Receiving Office (RO/US).

6. ■ A translation of the International Application into English (35 U.S.C. 371(c)(2)).

7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. □ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. □ have been transmitted by the International Bureau.
   c. □ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made.

8. □ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).

9. ■ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **(UNEXECUTED)**

10. □ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. □ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.

12. □ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.

13. ■ A FIRST preliminary amendment
    □ A SECOND or SUBSEQUENT preliminary amendment.

14. □ A substitute specification.

15. □ A change of power of attorney and/or address letter.

16. □ Other items or information:

"Express Mail Post Office to Addressee" service Mailing Label Number EL541613749US .

U.S. Application No. (If known, see 37 CFR 1.5) 09/857635	INTERNATIONAL APPLICATION NO. PCT/EP99/09404	ATTORNEY'S DOCKET NUMBER H 3243 PCT/US

17. ■ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....**$1,000.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....**$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37CFR 1.445(a)(2)) paid to USPTO **$710.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**

International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....**$100.00**

	CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).	$ 0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	22 - 20 =	2	2 X $18.00	$ 36	
Independent Claims	3 - 3 =	0	0 X $80.00	$ 0	
Multiple dependent claims (s)(if applicable)		0	+ $270.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 896	
Reduction of ½ for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ 0	
SUBTOTAL =				$ 896	
Processing fee of **$130.00** for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0	
TOTAL NATIONAL FEE =				$ 896	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$ 0	
TOTAL FEES ENCLOSED =				$ 896	
				Amount to be refunded:	$----------
				charged:	$896.00

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ■ Please charge my Deposit Account No. 50-1177 in the amount of $896.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. 01-0341 .

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-1177 . A triplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Cognis Corporation, Law Dept.
2500 Renaissance Blvd., Suite 200
Gulph Mills, PA 19406

SIGNATURE:

Aaron R. Ettelman
NAME ATTORNEY FOR APPLICANT

42,516
REGISTRATION NUMBER

"Express Mail " Mailing Label Number EL541613749US .

PATENT
Docket No. H 3243 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RE: PCT/EP99/09404
International Filing Date: December 2, 1999
Priority Date Claimed: December 9, 1998
Applicant: Lange, et al.
Title: AGENT AND METHOD FOR SEALING OR CONSOLIDATING ROCK, LOOSE ROCK OR SOILS, ESPECIALLY BORE HOLES
Applicants' Reference: H 3243 PCT/US

PRELIMINARY AMENDMENT

Commissioner for Patents
Box PCT
Washington, DC 20231

ATTN: DO/EO/US

Prior to the calculation of fees and examination of the above-identified national stage application pursuant to the accompanying submission under 35 U.S.C. §371, please amend the English translation of the International Application submitted herewith, without prejudice, as follows:

In the Specification:

Please amend the instant Specification, without prejudice, as follows:

Please delete all text above line 4 of page 1, and replace the deleted matter with the following new section headings and title of the invention:

--TITLE OF THE INVENTION

Rock and Soil Sealing Compositions Containing Silica Sols and Hardness Stabilizers, and Methods of Using the Same

BACKGROUND OF THE INVENTION--

At page 3, between lines 2 and 3 thereof, please insert the following new section heading and new paragraph:

Preliminary Amendment of U.S. National Stage for International Application PCT/EP99/09404 filed December 2, 1999

--BRIEF SUMMARY OF THE INVENTION

The present invention relates, in general, to compositions and processes for sealing or consolidating rock, mantle rock or soils and to the use for this purpose of silica sols containing hardness stabilizers.--

At page 3, between lines 19 and 20 thereof, please insert the following new section heading:

--DETAILED DESCRIPTION OF THE INVENTION--

At page 10, before line 1, please add the following new paragraph:

--What is claimed is:--.

On a separate, new page 12, following page 11, please add the following new section heading and paragraph containing an Abstract of the Disclosure:

--ABSTRACT OF THE DISCLOSURE

Compositions which comprise an aqueous silica sol and one or more hardness stabilizers selected from inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids, and polycarboxylics, are described for sealing and/or consolidating rocks and/or soils, particularly in digging or drilling applications. Methods of sealing and/or consolidating rocks and soils using said compositions are also described. --

In the Claims:

Please add new claims 11-32, as follows:

--11. (New) A composition comprising:

(a) an aqueous silica sol, wherein the composition contains SiO_2 in an amount of from 2 to 40% by weight based upon the weight of the composition; and

(b) from 0.01 to 400 ppm of a hardness stabilizer selected from the group consisting of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids, polycarboxylics, and mixtures thereof.--

--12. (New) The composition according to claim 11, wherein the aqueous silica sol comprises amorphous silica having an average particle size of from 1 to 150 nm and a specific surface value of from 50 to 700 m2/g.--

--13. (New) The composition according to claim 11, wherein the aqueous silica sol comprises amorphous silica having an average particle size of from 5 to 70 nm and a specific surface value of from 50 to 700 m2/g.--

--14. (New) The composition according to claim 11, wherein the aqueous silica sol comprises amorphous silica particles having surface-stabilizing hydroxyl groups.--

--15. (New) The composition according to claim 12, wherein the aqueous silica sol comprises amorphous silica particles having surface-stabilizing hydroxyl groups.--

--16. (New) The composition according to claim 11, wherein the hardness stabilizer is selected from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid and mixtures thereof.--

--17. (New) The composition according to claim 11, wherein the hardness stabilizer is present in an amount of from 0.1 to 200 ppm.--

--18. (New) The composition according to claim 11, wherein the hardness stabilizer is present in an amount of from 1 to 100 ppm.--

--19. (New) The composition according to claim 12, wherein the hardness stabilizer is selected from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid and mixtures thereof.--

--20. (New) The composition according to claim 12, wherein the hardness stabilizer is present in an amount of from 0.1 to 200 ppm.--

--21. (New) A method of sealing and/or consolidating loose and/or permeable materials, said method comprising:

(a) providing a material to be treated selected from the group consisting of rocks, mantle rock, soils, and mixtures thereof;

(b) contacting the material with an aqueous silica sol; and

(c) contacting the material with a hardness stabilizer selected from the group consisting of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids, polycarboxylics, and mixtures thereof.--

--22. (New) The method according to claim 21, wherein the material is contacted with the aqueous silica sol and the hardness stabilizer simultaneously in the form of a water-based composition comprising both the aqueous silica sol and the hardness stabilizer.--

--23. (New) The method according to claim 21, wherein the material is contacted with the aqueous silica sol, and subsequently contacted with the hardness stabilizer by adding the hardness stabilizer to the aqueous silica sol.--

--24. (New) The method according to claim 21, wherein the aqueous silica sol comprises amorphous silica having an average particle size of from 1 to 150 nm and a specific surface value of from 50 to 700 m2/g.--

--25. (New) The method according to claim 21, wherein the aqueous silica sol comprises amorphous silica having an average particle size of from 5 to 70 nm and a specific surface value of from 50 to 700 m2/g.--

--26. (New) The method according to claim 21, wherein the aqueous silica sol comprises amorphous silica particles having surface-stabilizing hydroxyl groups.--

--27. (New) The method according to claim 21, wherein the hardness stabilizer is selected from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid and mixtures thereof.--

--28. (New) The method according to claim 22, wherein the hardness stabilizer is present in the composition in an amount of from 0.01 to 400 ppm.--

--29. (New) The method according to claim 23, wherein the hardness stabilizer is added to the aqueous silica sol such that the hardness stabilizer is present in the sol in an amount of from 0.01 to 400 ppm.--

--30. (New) The method according to claim 22, wherein the hardness stabilizer is present in the composition in an amount of from 0.1 to 200 ppm.--

--31. (New) The method according to claim 23, wherein the hardness stabilizer is added to the aqueous silica sol such that the hardness stabilizer is present in the sol in an amount of from 0.1 to 200 ppm.--

--32. (New) A method of sealing and/or consolidating loose and/or permeable materials, said method comprising:

(a) providing a material to be treated selected from the group consisting

of rocks, mantle rock, soils, and mixtures thereof, wherein the material is in contact with water containing Ca^{2+} ions; and

(b) contacting the material with a composition comprising: (i) an aqueous silica sol, wherein the composition contains SiO_2 in an amount of from 2 to 40% by weight based upon the weight of the composition; and (ii) from 0.1 to 200 ppm of a hardness stabilizer selected from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid and mixtures thereof.--

Please cancel claims 1-10, without prejudice.

REMARKS

Claims 11-32 are currently pending in the instant application.

The Specification has been amended to delete the original section headings and to insert the preferred section headings pursuant to 37 C.F.R. §1.77. A new Title of the Invention has been inserted. An Abstract of the Disclosure, in accordance with the disclosure, has been added. It is submitted that the amendments to the Specification made herein introduce no new matter. All of the amendments to the Specification constitute deletions of original section headings and/or paragraphs, and insertions or additions of new section headings and/or paragraphs. Accordingly, pursuant to 37 C.F.R. §1.121(b)(1)(iii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. A separate page containing a clean copy of the Abstract of the Disclosure has been attached for the Examiner's convenience. Entry of the amendments to the Specification made herein are therefore proper and respectfully requested.

Original claims 1-10 have been canceled and replaced with new claims 11-32 solely for the purpose of improving clarity and grammar, which may suffer in translation, and not for any reason which relates to the statutory requirements for a patent. New claims 11-32 have not been added in response to any rejection, nor in anticipation of any rejection. Applicants respectfully submit that the scope of new claims 11-32 generally corresponds to the scope of original claims 1-10, and that new claims 11-32 are no narrower than original claims 1-10. Furthermore, although a moot point in view of their cancellation, Applicants respectfully submit that original claims 1-10 satisfied the requirements of 35 U.S.C. §112, as filed. New claims 11-32 are supported by the claims as originally filed and in the Specification, for example, at page 3, lines 5-13; at page 3, lines 20-29; at page 5, lines 10-16; and in the Examples. No new matter has been introduced. All of the amendments to the Claims constitute cancellation of original claims and the addition of new claims. Accordingly, pursuant to 37 C.F.R. §1.121(c)(1)(ii), no separate page captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE" is necessary. Entry is therefore proper and respectfully requested.

Preliminary Amendment of U.S. National Stage for International Application PCT/EP99/09404 filed December 2, 1999

Prompt examination of the instant application in view of the amendments made herein is respectfully requested.

Respectfully submitted,

ILONA LANGE, et al.

June 7, 2001
(Date)

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Agent and Method for Sealing or Consolidating Rock, Loose Rock or Soils, Especially Boreholes

This invention relates to a composition and a process for sealing or consolidating rock, mantle rock or soils and to the use for this purpose of certain silica sols containing hardness stabilizers.

The consolidation or sealing of rock, mantle rock or soils is a measure regularly necessary in construction engineering, for example for underpinning buildings, for sealing building pits or tips, in tunnel and canal construction and, above all, in geological exploration, such as the drilling of oil or natural gas pools. In the last of these applications, the sealing of wells is particularly important. Wells are sunk into the ground until a formation carrying oil, gas or - in well construction - water is reached. The well is stabilized against the formation by a cement casing. This cement casing is broken open at the bottom of the well so that the material to be brought up is able to pass freely from the formation into the well. Besides oil or gas, however, water also enters the well and has to be removed from the oil/gas by elaborate processes. Accordingly, efforts are made to minimize or avoid the penetration of water, so that the water-carrying parts of the formation are sealed off by suitable binders. However, consolidation or sealing is also a standard measure in the protection of agricultural land against wind or water erosion.

In general, binders, such as cement, bitumen, calcium salts or waterglass, are used in construction engineering. However, cement has the disadvantage that the particles are often not small enough to be able to penetrate into fine cracks or pores, resulting in an unsatisfactory sealing or consolidating effect. Even the use of waterglasses (an aqueous solution of sodium silicate) or microsilicas (an aqueous dispersion of amorphous silicon dioxide) does not always produce the required sealing effect. Accordingly, **EP 530 600** proposes the use of silica sols for sealing or

consolidation. Silica sols are colloidal solutions of amorphous silicon dioxide which has a particle size of 7 to 50 nm. These silica sols gel in the presence of certain electrolytes or in the event of changes in the pH of the aqueous sols. By crosslinking of the SiO_2 units, the gel becomes more viscous until consolidation is complete. Electrolytes which initiate gelation are generally present in the material to be consolidated or sealed. They are preferably salts of aluminium, iron, calcium or magnesium. However, EP 0 530 600 A1 proposes using silica sols in combination with a calcium donor in order to achieve rapid conversion of the sol into the gel.

Now, applicants have found that, surprisingly, the use of silica sols does not always lead to the required sealing or consolidating effects. This is particularly the case in the sealing of wells against penetrating formation water. According to applicants' observations, a free water phase frequently occurs which is a sign that no gelation and hence no sealing has taken place. Accordingly, without being confined to one particular theory, applicants assume that, in contrast to the teaching of EP 0 530 600 A1, the formation of alkaline earth metal silicates and, above all, calcium silicate can inhibit the gelation process. Accordingly, one of the problems addressed by the present invention was to provide a sealing or consolidating process which could even be carried out in the presence of water containing alkaline earth metal ions.

In addition, it is often not desirable in the sealing of wells to achieve rapid solidification of the binder. The binder is transported under pressure to the bottom of the well through a suitable pipe and is forced into the formation there. The effect of rapid solidification of the binder would be that the binder would also gel in the pipe itself which of course is not what is wanted. On the contrary, the gelling effect should be delayed to the extent that the entire binder is forced into the formation by flushing, for example with water, so that gelation and consolidation only occur in the required places. Accordingly, another problem addressed by the present invention

was to provide a process for the delayed consolidation or sealing of rock, mantle rock or soils.

It has now surprisingly been found that a mixture of aqueous silica sol and certain inhibitors for Ca^{2+} ions solves the problems stated above.

In a first embodiment, the present invention relates to a water-based composition for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, the composition containing 2 to 40% by weight of SiO_2 (dry matter, based on the composition) in the form of an aqueous silica sol and, in addition, hardness stabilizers from the class of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids and polycarboxylic acids or mixtures of these substances in concentrations of 0.01 to 400 ppm.

The compositions according to the invention are generally suitable both for the consolidation and for the sealing of any type of rock, mantle rock or soils in contact with water containing Ca^{2+} ions. Typical applications include construction engineering, particularly tunnel and well construction, and geological exploration, more particularly the sealing of wells, more precisely their walls, against penetrating formation water.

Besides water, the compositions according to the invention contain silica sols containing amorphous SiO_2 in quantities of 2 to 60% by weight, expressed as dry matter and based on the sol, as carrier liquid. However, silica sols containing 25 to 50% by weight amorphous SiO_2 are preferred for the compositions according to the invention. The amorphous SiO_2 is present in the form of non-interlinked spherical individual particles surface-stabilized by hydroxyl groups. The average particle diameter is in the range from 1 to 150 nm, preferably in the range from 5 to 70 nm and more particularly in the range from 5 to 40 nm. The specific surface of the silica sols is in the range from 50 to 700 m^2/g, as measured by the BET method. By virtue of the colloidal distribution of the particles, no sedimentation of

particles is observed with silica sols. Accordingly, the sols may be stored for years. Aqueous silica sols are generally used. However, amorphous SiO_2 may also be converted into sols in other solvents, for example acetone or short-chain organic alcohols, such as methanol, ethanol or propanol (cf. **Ullmanns Encyklopädie der Technischen Chemie, 4th Edition, Vol. 21, pages 456 to 463, Weinheim 1982**). However, the compositions according to the invention contain only aqueous silica sols.

The compositions according to the invention contain in all, i.e. including the water content of the silica sols, between 60 and 98% by weight and more particularly between 60 and 80% by weight of water which preferably contains only small amounts of electrolytes, for example between 0.001 and 0.1% by weight. The water is preferably free from electrolytes. Electrolytes in the present context are understood in particular to be cations of mono- and divalent alkali metal and alkaline earth metal ions, i.e. Na^+, K^+, Ca^+ and Mg^{2+} ions. Aqueous silica sols of the type described above are present in the compositions in quantities of 20 to 60% by weight. According to the invention, so-called hardness stabilizers are added to the mixture of silica sol and water in concentrations of 0.01 to 400 ppm. Hardness stabilizers are compounds which, in less than stoichiometric quantities known for the purpose, are capable of completely and permanently preventing the precipitation of hardness ions from supersaturated aqueous solutions. To this extent, it was surprising that the addition of these compounds only leads to delayed gelation of the silica sols but does not permanently suppress their gelation. Hardness ions are mainly alkaline earth metal ions, more particularly calcium and magnesium ions (threshold effect). Particulars can be found in **Römpps Chemie Lexikon, 9th Edition, Vol. 6, 1994, pages 5000 to 5002**.

The compositions according to the invention contain compounds from the class of inorganic polyphosphates, phosphonic acid, aminoethylene phosphonic acids, phosphoric acid esters,

phosphonocarboxylic acids and polycarboxylic acids or mixtures thereof as hardness stabilizers. Salts of these compounds are also suitable. Compositions containing hardness stabilizers from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid, polyaspartic acid, polymaleic acid or derivatives thereof or mixtures of these compounds are particularly preferred. Compositions containing tetrakis-[(phosphono-methyl)-imino]-bis-[2,1-ethanediylnitrido-bis-methylene]-phosphonic acid and/or salts thereof as hardness stabilizers are most particularly preferred.

Preferred mixtures of these stabilizers contain, for example, 1-hydroxyethane-1,1-diphosphonic acid sodium salt and polyacrylic acid or 1-hydroxyethane-1,1-diphosphonic acid sodium salt, aminotris-(methylenephosphonic acid) and polyacrylic acid. The concentration in which the hardness stabilizers are used is between 0.01 and 400 ppm, more particularly in the range from 0.1 to 200 ppm and preferably in the range from 1 to 100 ppm, based on hardness stabilizer active substance.

In another embodiment, the present invention relates to a process for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, in which the material to be consolidated or sealed is contacted with a solution containing aqueous silica sol and hardness stabilizers from the class of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphono-carboxylic acids and polycarboxylic acids or mixtures of these substances.

Aqueous silica sols containing 20 to 60% by weight SiO_2 (dry matter, based on the aqueous sol) are preferably used for this purpose. In general, the composition is forced under pressure into the material to be sealed or consolidated. The hardness stabilizers are then added during or after the treatment with the silica sol. They are preferably used in such quantities that the stabilizer concentration, based on the aqueous silica sol solution, is in the range from 0.01 to 400 ppm, preferably in the range from

0.1 to 200 ppm and more particularly in the range from 1 to 100 ppm.

In one particularly preferred embodiment, the process according to the invention is used for sealing underground formations, more particularly wells. To this end, the silica sol/water/stabilizer mixture is pumped through the feed pipe by suitable pumps to the bottom of the well, such a pressure being applied that the mixture penetrates deeply into the formation. This is followed by flushing with water until the mixture has been completely removed from the pipe. In this connection, the process according to the invention enjoys another advantage because the composition used only gels with a certain delay. Under the temperature, pH and pressure conditions at the bottom of the well, the composition preferably solidifies some 30 to 60 minutes after contacting with the material to be consolidated or sealed and hence with the water containing Ca^{2+} ions. The temperatures at the bottom of the well are normally in the range from 30 to 200°C, depending on the depth. The pressure is typically between 10 and 500 bar, again dependent on depth.

The most suitable stabilizer concentration can be selected in dependence upon the concentration of Ca^{2+} ions in the water with which the material to be consolidated or sealed is in contact. It has been found that the hardness stabilizers should preferably be present in the compositions according to the invention in such quantities that, based on a predetermined volume, the ratio by weight of Ca^{2+} ions to the hardness stabilizers is in the range from 0.5 to 5.0:1. The quantity of Ca^{2+} ions may readily be calculated through the determination of the water hardness.

The water in contact with the material to be consolidated or sealed generally has a content of Ca^{2+} ions of greater than 2 mmol/l and preferably greater than 4 mmol/l. Typical Ca^{2+} concentrations are in the range from 3 to 8 mmol/l. The pH of the formation water is generally in the acidic to mildly alkaline range, i.e. between 6 and 9. It has been found that a reduction in pH to values of 2 to 5 can generally prevent gelation.

Accordingly, the process according to the invention is preferably carried out at pH values of 6 to 9 or the composition according to the invention is preferably formulated by addition of acids or bases in such a way that its pH value is in the range mentioned.

The present invention also relates to the use of the compositions described in the foregoing for consolidating or sealing rock, mantle rock or soils in contact with water containing Ca^{2+} ions.

Examples

The effectiveness of the process according to the invention was determined as follows: 11 g of a silica sol (Köstrosol® 0830 of Chemiewerk Bad Köstritz) were mixed with 40 g of deionized water and hardness stabilizers were subsequently added to the sol in various quantities. Between 0.7 and 1.0 ml of a calcium chloride solution (concentration of Ca^{2+} ions: 28,200 ppm) was then added dropwise to the resulting mixture, followed by heating for 15 minutes to 100°C. The vessel was left standing without stirring to cool. After 30 minutes, the degree of gelation was visually determined.

The following evaluation was made:

100% solid	++
80 to almost 100% solid	+
less than 80% solid	-

The following hardness stabilizers were tested:

A: 1-hydroxyethane-1,1-diphosphonic acid

B: amino-tris-(methylene phosphonic acid)

C: 1-hydroxyethane-1,1-diphosphonic acid disodium salt

D: mixture of B and C and polyacrylic acid

The stabilizers were used in the form of commercially available aqueous solutions (all products of Henkel KGaA):

A: 60% by weight active substance (Turpinal® SL)

B: 50% by weight active substance (Turpinal® D2)

C: 10% by weight active substance (Turpinal® -2-NZ)

D: 30% by weight active substance (Fostex® 617 B)

The quantities in Table 1 are based on active substance.

The results of the tests are set out in Table 1.

Table 1

No.	Stabilizer	Stabilizer concentration [ppm]	$CaCl_2$ solution [ml]	Ca^{2+} content in the solution [% by weight]	Ratio by weight Ca^{2+}:stabilizer	Gelation after 30 mins.
1	A	0.1	0.8	0.04	0.7	++
2	A	0.2	0.8	0.04	1.0	++
3	B	0.3	0.8	0.04	1.4	+
4	B	0.3	0.7	0.04	2.0	++
5	C	0.7	1.0	0.06	1.3	++
6	C	0.7	1.0	0.06	1.5	+
7	D	0.7	1.0	0.06	4.0	++

Tests were also carried out at elevated temperature and pressure in order to simulate the conditions prevailing at the bottom of the well. Quantities of 5 g of a 50% by weight aqueous silica sol were diluted with 45 g of water and a certain ratio by weight of Ca^{2+} to SiO_2 was then adjusted by addition of a $CaCl_2$ solution (0.04% by weight Ca^{2+}). The system was then heated for 30 minutes to 150°C in an autoclave under 10 bar pressure (nitrogen atmosphere) and left under those conditions for two hours. The results of the visual evaluation of the solutions are set out in Table 2.

Table 2

Solution	Ca:SiO_2 [% by weight]	Effect
8	0.005	Thinly liquid
9	0.010	Slight gelation
10	0.020	Gelation
11	0.030	Gelation

Various quantities of stabilizer D were then added to solution 10 under the described conditions. It was found that the addition of 100 and 200 ppm of stabilizer resulted in delayed gelation after three hours. At higher concentrations, there was no sign of gelation. Accordingly, the process according to the invention leads to a desired delay in the gelation of the silica sol solutions, even at elevated temperature and pressure.

CLAIMS

1. A water-based composition for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, the composition containing 2 to 40% by weight of SiO_2 (dry matter, based on the composition) in the form of an aqueous silica sol, characterized in that it contains hardness stabilizers from the class of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids and polycarboxylic acids or mixtures of these substances in concentrations of 0.01 to 400 ppm.

2. A composition as claimed in claim 1, characterized in that the hardness stabilizers are selected from the group consisting of aminotris(methylenephosphonic acid), 1-hydroxyethane-1,1-diphosphonic acid, phosphonobutane tricarboxylic acid, polyacrylic acid or mixtures of these compounds.

3. A composition as claimed in claim 1 or 2, characterized in that it contains the hardness stabilizers in concentrations of 0.1 to 200 ppm and preferably in concentrations of 1 to 100 ppm.

4. A process for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions, in which the material to be consolidated or sealed is contacted with a solution containing aqueous silica sol and hardness stabilizers from the class of inorganic polyphosphates, phosphonic acids, aminoethylene phosphonic acids, phosphoric acid esters, phosphonocarboxylic acids and polycarboxylic acids or mixtures of these substances.

5. A process as claimed in claim 4, characterized in that aqueous silica sols containing 20 to 60% by weight of SiO_2 and preferably 25 to 50% by weight of SiO_2 (dry matter, based on the aqueous sol) are used.

6. A process as claimed in claim 4 or 5, characterized in that the hardness ions are added in such quantities that their concentration in the aqueous silica sol solution is between 0.01 and 400 ppm, preferably

between 0.1 and 200 ppm and more particularly between 1 and 100 ppm.

7. A process as claimed in any of claims 4 to 6, characterized in that the material to be consolidated or sealed is in contact with water having a concentration of Ca^{2+} ions of more than 2 mmol/l

8. A process as claimed in any of claims 4 to 7, characterized in that it is used to seal underground formations, preferably wells.

9. A process as claimed in any of claims 4 to 8, characterized in that the consolidating or sealing effect begins 30 to 60 minutes after contacting of the composition with the material to be consolidated or sealed.

10. The use of the compositions claimed in any of claims 1 to 3 for sealing or consolidating rock, mantle rock or soils in contact with water containing Ca^{2+} ions.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number	H 3243 PCT/US
First Named Inventor	LANGE, Ilona
COMPLETE IF KNOWN	
Application Number	09/857,635
Filing Date	11/09/2001
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:
My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

AGENT AND METHOD FOR SEALING OR CONSOLIDATING ROCK, LOOSE ROCK OR SOILS, ESPECIALLY BORE HOLES

(Title of the Invention)

the specification of which
☐ is attached hereto
OR
☒ was filed on (MM/DD/YYYY) 12/02/1999 as United States Application Number or PCT International Application Number PCT/EP99/09404 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
198 56 729.4	DE	12/09/1998	☐	☐	☒

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)

☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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DECLARATION

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*
	PCT/EP99/09404	12/02/1999	

[ ] Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Type a plus sign (+) inside this box [ ]

H 3243 PCT/US

DECLARATION

ADDITIONAL INVENTOR(S) Supplemental Sheet

2-00

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☐ Additional inventors are being named on supplemental sheet(s) attached hereto